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## Chemical Characterization and Toxicologic Evaluation of Airborne Mixtures

## Chemical Characterization of Combusted Inventory Red and Violet Smoke Mixes

FINAL REPORT

I. B. Rubin  
M. V. Buchanan  
J. H. Moneyhun

OCTOBER 1982

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U.S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND  
Fort Detrick, Frederick, MD 21701

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19. 2-Methylaminoanthraquinone      Thin layer chromatography  
NMR      X-ray diffraction  
Signalling      X-ray fluorescence  
Smoke  
Spectrometry
20. formulated to contain 1,4-diamino-2,3-dihydroanthraquinone (DAA) and MAA. Upon combustion the DAA was converted almost completely to diaminoanthraquinone (DAA) which was a minor constituent of the uncombusted mix. As in the combusted red smoke mix, it was found that MAA was partially converted to aminoanthraquinones.

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Chemical Characterization and Toxicologic Evaluation of  
Airborne Mixtures

CHEMICAL CHARACTERIZATION OF COMBUSTED INVENTORY  
RED AND VIOLET SMOKE MIXES

FINAL REPORT

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Date Published: July 1983

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## EXECUTIVE SUMMARY

To compare the composition of smoke mixes used in red and violet smoke grenades before and after combustion, smoke mixes which were from the same lot as those in the smoke grenades were obtained, separated and analyzed as described previously.<sup>(1,2)</sup> Because of the necessity to collect enough material for both biological and chemical testing, a whole grenade was used to generate the combusted material. Environmental regulations restricted the open detonation of a smoke grenade, so a conventional family-sized camping tent was used as the combustion chamber. The tent was greater than 99% efficient in containing the smoke generated when the window flaps were sealed. Particulate and vapor phase samples were drawn out of the tent through Teflon tubing sampling ports by a number of sampling pumps and collected in a variety of traps and filters.

Because of the addition of the inorganic combustion mixtures to the dyes,<sup>(3)</sup> and because of the chemical modifications of the dyes themselves, the procedures used for the analysis of the original smoke mixes had to be modified, or new procedures devised in order to analyze the combusted dye mixes effectively. The separation of the particulate matter from the combusted smoke mixes into fractions suitable for chemical analysis was accomplished by open column chromatography on silica gel, although the red smoke mix was also fractionated by vacuum sublimation. The resultant fractions were characterized primarily by combined gas chromatography/mass spectrometry. Silica gel chromatography gave excellent separation of the major constituents and allowed concentration of the impurities into several fractions. The unsublimed residue from the vacuum sublimation procedure was examined by microscopic and x-ray techniques. Vapor phase samples were collected on Tenax and XAD-2 traps, and were analyzed by combined gas chromatography/mass spectrometry after either thermal desorption or extraction from the resin. The particle size distribution of the airborne particulates was determined after collection in an 8-stage cascade impactor and the mass median diameters calculated.

The impact of the detonation on the red smoke mix was slight. The single dye component, 1-methylaminoanthraquinone was reduced from 98 percent of the chloroform soluble portion of the original mix to 86 percent in the combusted mix, with apparent conversion to 1- and 2-aminoanthraquinones being the major factor in this change. The residue portion of the combusted red smoke mix contained sodium and potassium chlorides, elemental sulfur and undifferentiated carbonaceous matter in contrast to only the carbonaceous matter and some dye in the original mix residue. The violet smoke mix underwent a drastic change during combustion, with the 1,4-diamino-2,3-dihydroanthraquinone, which was the major constituent of the original smoke mix, being quantitatively converted to 1,4-diaminoanthraquinone. Only a small proportion, about 4 percent, of the particulates of both mixes were water soluble.

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The objective of this study was to combust under actual use conditions two colored smoke grenades, red and violet, collect both particulate and vapor phases, and separate and identify the major components present. Portions of the fractions obtained from the particulate phase were to be sent to the ORNL Biology Division for biological testing as well. Because the geometry of the grenade has been shown to affect the temperature profile of the burn, it was necessary that a whole M18 smoke grenade be used to generate the combusted material. Dye mixes which were used in the manufacture of the smoke grenades were also obtained and were to be fractionated and characterized as described previously<sup>(1,2)</sup> for comparison with the combusted smoke mixes.

Because of the addition of inorganic components to the smoke mixes in the smoke grenades<sup>(3)</sup> as well as the chemical modifications of the dyes themselves due to combustion, the procedures used for the analyses of the original smoke mixes<sup>(1,2)</sup> had to be modified, or new procedures devised in order to analyze the combusted dye mixes effectively. The separation methods used as well as the chemical composition of the resulting fractions are described. In addition, the vapor phase constituents and the average particle size of the smoke aerosols are reported. Detailed information on the fractionation procedures, elemental analyses, vapor phase analyses and particle size determinations are given in Appendices A, B, C, and D, respectively.

MATERIALS AND METHODSDye and Smoke Materials

Standard dye materials were supplied by the U. S. Army Armament Research and Development Command, Aberdeen Proving Ground, Maryland, courtesy of R. G. Grafton, Chief, Chemical Systems Division, Product Assurance Directorate. These included 1-methylaminoanthraquinone (MAA) [1(methylamino-9,10-anthracenedione, CAS 82-38-2)] and 1,4-diamino-2,3-dihydroanthraquinone (DDA) [1,4-diamino-2,3-dihydro-9,10-anthracenedione, CAS 81-63-0]. 1,4-Diaminoanthraquinone (DAA) [1,4-diamino-9,10-anthracenedione, CAS 128-95-0] was prepared by separation from a chloroform solution of DDA by preparative scale thin layer chromatography. Red and violet M18 colored smoke grenades, and the smoke mixes from which they were made, red smoke mix lot no. THF-4-26 and violet smoke mix lot no. RJC-31-123, were obtained from Pine Bluff Arsenal through the courtesy of CPT. David Johnson of the U. S. Army Medical Bioengineering Research and Development Laboratory. The red smoke mix is formulated to contain 100 percent MAA, while the violet smoke mix is formulated to contain 80 percent DDA and 20 percent MAA. The red and violet grenades contain 40 percent and 42 percent of the smoke mix, respectively, along with a combustion mixture of sodium bicarbonate, potassium chlorate and sulfur. The grenades also contain a starter mix of potassium nitrate, sulfur, sodium bicarbonate and corn starch.<sup>(3)</sup>

Combustion and Sampling. The red and violet smoke hand grenades were detonated in separate 9 x 11 x 6 2/3 ft Hillary family tents

(Sears, Roebuck, Catalog No. 6G77105C) which were used as combustion and sampling chambers. The window flaps were taped shut to prevent escape of the smoke into the atmosphere. The grenades were clamped over a galvanized tub which contained gravel to prevent ignition of the floor material. The grenades were detonated remotely using a pull cord tied to the pin. As soon as the fuse was detonated, the door flap was closed.

Sampling ports of Teflon tubing were inserted in the tents through slits and were secured. Particulate matter was collected in a 43 x 123 mm fiber glass extraction thimble that had been previously washed overnight with methylene chloride in a Soxhlet extractor. The thimble was held in an Anderson stainless steel filtering thimble holder (Anderson Samplers, Inc., Atlanta, GA) with the air being pulled through at a rate of  $\sim 120$  L/min by a 1/2 HP Doerr Carbon Vane pump (Doerr Electric Co., Cedarburg, WI). A Mine Safety Appliance (Pittsburgh, PA) type H ultra filter cartridge was used to back up the extraction thimble. Particulate matter fallout was collected in four 30 x 45 cm glass trays placed on the floor of the tent. A total of  $\sim 9$  g of red smoke and 5 g of violet smoke were recovered from the sampler and trays.

Samples for particle size determination were collected by a Mercer-Lovelace seven stage cascade impactor (In-Tox Products, Albuquerque, NM) by means of a Dyna-Vac laboratory pump (Cole-Parmer, Chicago, IL) at 1 L/min. Samples were collected from the red smoke test for 1 min and for 10 sec at 7 and at 26 min after ignition, respectively. Samples were collected from the violet smoke test for 15 sec each at 2 and 28 min after ignition. Vapor phase samples were adsorbed on pretreated Amberlite XAD-2 (Polysciences, Warrington, PA) and on Tenax-GC (Applied Science Division, Milton Roy Laboratory Groups, State College, PA). A standard Cambridge fiber glass filter pad was used to exclude particulate matter. Sampling rate was  $\sim 1.5$  L/min using a Dupont Model P4000 air sampling pump (E.I. DuPont de Nemours, Applied Technology Division, Wilmington, DE). The vapor phases were sampled for ten minute periods starting at about three and thirty minutes after ignition.

Separations and Chemical Characterization. The original (uncombusted) smoke mixes were fractionated by previously described procedures.<sup>(1,2)</sup> The combusted red smoke mix was fractionated by a slight modification of the vacuum sublimation procedure which was used previously<sup>(1,2)</sup> as described in Appendix A. Separation by vacuum sublimation was accomplished using a standard sublimation apparatus immersed in a heated oil bath. The reduced pressure (100 mtorr) was obtained with a rotary vacuum pump. The volatile fractions were collected at the indicated temperature for five hours, and were washed off the water cooled condenser with glass-distilled chloroform. Thimbles for Soxhlet extractions (no. 603 from Schleicher and Schuel) for the differential solubility procedure<sup>(1,2)</sup> were extracted overnight with chloroform prior to use. In order to obtain an improved separation of the major constituents, and to concentrate the impurities into more distinct fractions, both the combusted red and violet smoke mixes were chromatographed by open column liquid chromatography on silica gel columns. The original (uncombusted) red smoke mix was chromatographed similarly. Davison Chemical Co. (Baltimore, MD) silica gel, grade 950, 60-200 mesh was used for column chromatography without pretreatment.

Brinkman Instruments (Westbury, NY) SIL-N-HR (0.20 mm) silica plates were used for analytical scale thin layer chromatography (TLC). Brinkman SIL-G-200 UV<sub>254</sub> (2.0 mm) plates were used for preparative-scale TLC. The developing solution was chloroform/methylethylketone/glacial acetic acid (60/80/1). The TLC plates were examined by ultraviolet light at 254 and 366 nm as well as by visible light.

Gas chromatographic measurements were made using either a Hewlett-Packard Model 5840A gas chromatograph with a 25 meter methyl silicone coated fused silica capillary column (Quadrex Corp., New Haven, CT) or a Perkin-Elmer Model 3920 gas chromatograph with a 30 meter FB-5 bonded fused silica capillary column (Quadrex). Both gas chromatographs were equipped with flame ionization detectors with hydrogen and air pressures at 20 and 30 psig, respectively. Helium was used as the carrier gas at 30 psig head pressure. Temperature programming varied according to the type of sample.

Spectroscopic Measurements. Visible and ultraviolet spectra were obtained using a 1-cm cell in a Varian Model DSO 90 double beam recording spectrophotometer. Samples were measured at concentrations of 0.20 to 0.25 mg/mL for visible spectra and 0.005 to 0.010 mg/mL for ultraviolet spectra with chloroform as the solvent. Particle size determinations were based on spectrophotometric measurements at 508 nm for the red smoke and 542 nm for the violet smoke. A chloroform solution of the whole combusted smoke mix was used as the reference standard in each case.

Proton (<sup>1</sup>H) and carbon (<sup>13</sup>C) nuclear magnetic resonance (NMR) spectra were obtained at 89.56 MHz and 22.50 MHz, respectively, using a JEOL FX90Q Fourier transform NMR spectrometer. The spectra were run at an ambient probe temperature of 28°C, with internal deuterium lock. The samples were run in deuterated chloroform with tetramethylsilane (TMS) (Aldrich Chemical Co., Milwaukee, WI) added as an internal reference. The proton spectra were run using a 28-μs (90°) pulse, and a 5-s pulse delay for four scans. The carbon spectra were run using an 11.5-μs (45°) pulse angle and a 15-s pulse delay. The spectra were accumulated overnight with ~4000 scans.

Mass spectra were obtained with a Hewlett-Packard 5985A gas chromatograph/mass spectrometer (GC/MS), with the electron impact source at 70 eV. Ammonia and ammonia-d<sub>3</sub> were used as chemical ionization reagents at 0.1-0.2 torr at 200 eV.<sup>(4)</sup> Soluble samples were introduced via the gas chromatograph interfaced to the mass spectrometer. The gas chromatograph was equipped with a fused silica capillary column coated with either OV-101 (SGE, Austin, TX) or methylphenylsilicone (Quadrex). The carrier gas was helium at 30 psig head pressure. The inlet and GC/MS transfer lines were held at 280°C. The oven temperature was programmed from 100° to 250°C at a 5°C/min rate, and with a 5 min holding period at the initial temperature. Splitless sample injection was used. The non-soluble samples were introduced into the mass spectrometer via a direct insertion probe (DIP) which was programmed from 20° to 200°C at a 10°/min rate and with a 5 min holding period at the initial temperature.

The vapor phase samples from the XAD-2 traps were extracted overnight in a Soxhlet extractor, concentrated, and injected into the GC/MS

by normal splitless injection. The gas phase samples from the Tenax traps were analyzed directly by GC/MS by thermal desorption.<sup>(5)</sup> These vapor phase sample procedures are described in detail in Appendix C.

## RESULTS AND DISCUSSION

### COMBUSTION AND SAMPLING

The combustion and sampling of the signal smoke grenades were designed to take place in an enclosure to prevent escape of aerosols into the environment as required by local, state, and federal environmental regulations. The use of a medium size tent as the combustion and sampling chamber was the most convenient and economical of the options considered. The camping tent used in these tests was moderately priced, easily obtainable, could be erected by two people in about fifteen minutes, and was stable enough to be left up under adverse weather conditions for several weeks. When testing was completed, the tent was easily collapsed, boxed and disposed of. These tents have two rolldown window flaps which were taped shut, and a zippered door flap. During the grenade tests, only traces of smoke were observed escaping the tent, and those mainly when a gust of wind would hit the side of the tent causing a small, momentary rise in the interior pressure. A preliminary test using a red smoke grenade was carried out in order to check out the sampling equipment and procedures. During this test, the interior of the tent was observed from time to time, and it was noted that the particulates remained airborne and eddying for more than an hour, and that a substantial amount of particulates were collecting on the floor of the tent. Consequently, it was decided to place several glass trays on the floor of the tent to collect more particulates.

For the combustion tests, the grenades were clamped onto a bar over a galvanized tub of gravel. This stabilized the grenades and prevented accidental burning of the tent floor. The grenades were detonated remotely by a pull cord tied to the pin, and the door flap was zippered shut as soon as ignition was complete, and before any smoke could escape. Cords were attached to the glass trays so that they could be pulled to the door and removed without personnel entering the tent. The glass trays were removed from the tent about four hours after the test began to allow the particulates to settle completely. They were wrapped in aluminum foil and taken back to the laboratory for emptying. For the red smoke test, about five grams of sample were recovered from the high volume sampler and four grams from the trays. The violet particulates were considerably less dense than the red, and only two grams were recovered from the sampler, and an equal amount from the trays.

The tents were erected in an open field so that the prevailing winds would carry any escaping smoke away from any occupied buildings. The tests were carried out on sunny, clear days when the ambient temperatures were in the mid to high forties and the relative humidity was in the region of 30 percent. At test time, the interior of the tents

was about ten to twelve degrees warmer than ambient because of solar heating, and the interior temperatures undoubtedly continued to rise more than exterior temperatures, which would contribute to the convective currents keeping the particulates airborne. All safety precautions were taken including protective clothing, face shields and dust respirators. A fire hose was provided for the preliminary test, but in subsequent tests fire extinguishers were considered adequate. When the tests were completed, the galvanized tubs were removed from the tents and were double wrapped in large plastic bags. The tents were then struck, folded and also double wrapped in plastic bags. Only very small amounts of dyes were spilled on the grass during these operations. The tubs and tents were then taken to be buried by the laboratory disposal squad.

#### CHEMICAL CHARACTERIZATION OF COLORED SMOKE MIXES

##### Red Smoke Mix

Uncombusted. The red smoke mix is formulated to contain only one dye component, 1-methylaminoanthraquinone (MAA).<sup>(3)</sup> The uncombusted red smoke mix (Lot THF-4-26) was first fractionated by vacuum sublimation by the method previously described.<sup>(1,2)</sup> The gravimetric analysis of the fractions from this test mix was very similar to that of the original smoke mix (RSM) as is shown in Table 1. The ultraviolet and visible spectra of fractions 1 and 2 were identical to those of the 1-methylaminoanthraquinone standard. Spectrophotometrically, both fractions were 100% pure MAA. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of fraction 2 were identical with those of the MAA standard. When fractions 1 and 2 were examined by TLC, there was an orange fluorescent band (254 nm) just below the main MAA band in each fraction, but no other impurities were observed. The whole red smoke mix left a faint red band at the origin. These two fractions were also analyzed by combined GC/MS. Fraction 1 was predominantly MAA along with a minor amount of anthraquinone, while fraction 2 contained only MAA, and no detectable impurities. Fraction 3 was light purple in color rather than black as in the RSM. Direct probe mass spectral analysis of fraction 3 revealed that this fraction contained some MAA along with hydrocarbon residues. No further analysis of fraction 3 was carried out due to its non-volatile and non-soluble nature.

Subsequent analysis of the combusted smoke mix, as discussed below, indicated the presence of a fairly large impurity. Because of the effectiveness of TLC on silica gel plates in separating components of the smoke mixes, an open column chromatographic separation on silica gel was tested and found to be successful. Therefore, a similar chromatographic separation of the chloroform soluble portion of the uncombusted red smoke mix was carried out in order to get a better comparison between the combusted and uncombusted mixes than was afforded by the vacuum sublimation procedure. Separation into bands was decided by color. Band 1 was red, band 2, orange, and band 3 was the remainder of the material eluted by chloroform. Band 4 was the material elutable by acetone.

TABLE 1. COMPARATIVE WEIGHT FRACTIONS OF COLORED SMOKE MIXES BY THE ORIGINAL SEPARATION PROCEDURES

Fraction	Percent of Total			
	Red Smoke Mixes		Violet Smoke Mixes	
	RSM <sup>a</sup>	THF-4-26	VSM <sup>a</sup>	RJC-31-123
1	11.7	14.3	17.9	17.9
2	73.6	70.5	3.6	4.2
3	12.7	13.4	52.6	53.3
4	--	--	24.3	23.7
Total	98.0	98.2	98.4	99.1

<sup>a</sup>Data from Rubin and Buchanan

The gravimetric results of the chromatographic separation are shown in Table 2. These bands were analyzed by GC/MS only. Band 1 was deep red color and contained only MAA with no detectable impurities. Band 2 contained aminoanthraquinone (AA) as the major constituent with a small amount of MAA. Because of the orange color of the solution, the major constituent was most likely 1-AA.<sup>(6)</sup> The major impurity in band 2 appeared to be a hydrocarbon (possibly in the C<sub>10</sub> range) while there were several other minor impurities including some siloxanes. As can be seen in Table 2, this fraction represented less than 1 percent of the total. The two major components of band 3 were AA and an aliphatic amide whose molecular weight is unknown. About twelve other minor impurities were detected and they appeared to be other amides as well as hydrocarbons. As shown in Table 2, this band represented slightly more than 1 percent of the total. Thus, from these data, the chloroform soluble portion of this smoke mix was found to be approximately 98 percent MAA.

TABLE 2. SILICA GEL COLUMN CHROMATOGRAPHY OF COLORED SMOKE MIXES

Band	Portion of Sample Chromatographed, %		
	Original	Combusted	Combusted
	Red Smoke	Red Smoke	Violet Smoke
1	98.1	85.6	28.1
2	0.6	6.4	3.5
3	1.3	6.4	1.1
4	0.0	3.4	64.4
5	--	--	11.7
Total	100.0	101.8	108.8

Combusted. The M18 colored smoke grenades are filled with a mixture of about 40 percent of the colored smoke mix with about 25 percent each of sodium bicarbonate and potassium chlorate and 9 percent sulfur.<sup>(3)</sup> In addition, each grenade contains 50 g of a starter mix of sodium bicarbonate, potassium nitrate, sulfur and a small amount of nitrocellulose binder. Consequently, the combustion products of the exploded grenade might be expected to contain a number of compounds not observed in the non-combusted smoke mix.

The particulate products from the grenades were collected using both a high volume sampler and glass trays as described in the Materials and Methods section above. The solids were first subjected to the vacuum sublimation procedure described previously.<sup>(1,2)</sup> Several differences from the results of a similar procedure for the uncombusted smoke mix were immediately apparent. In fraction 2, there was an orange substance overlaying the red MAA layer, which indicated the presence of a material with a higher sublimation temperature than the MAA. When fraction 2 was dissolved from the condenser, a thin yellow layer remained that was completely soluble only in dimethylsulfoxide. Finally, the residue, fraction 3, was a compact blackish material as compared to the fluffy purple residue from the uncombusted smoke mix. In order to concentrate the orange impurity, the vacuum sublimation procedure was modified slightly and fraction 2 was subdivided into two subfractions. The yellow insoluble layer on the condenser was then labeled fraction 4. The schematic flow sheet for the modified vacuum sublimation procedure is shown in Appendix A, Figure A-1, and the proportions of the fractions are also shown. These fractions were analyzed only by GC/MS (fractions 1, 2a and 2b) and direct probe MS (fractions 3 and 4). Fraction 1 was almost pure MAA with very minor amounts of sulfur and AA present. Fraction 2a was almost pure MAA, with a very small amount of AA present again. The major component of fraction 2b was AA, and because of the orange color of the solution, probably 1-AA.<sup>(6)</sup> There was a substantial amount of MAA in fraction 2b, as well as a significant amount of sulfur.

Fraction 3, the unsublimed residue, was divided into water soluble and water insoluble portions. The water insoluble portion was examined by direct probe mass spectrometry and was found to contain mainly hydrocarbon residues with some elemental sulfur. Both portions were examined by microscopy and x-ray techniques. The water soluble portion contained mainly sodium and potassium chlorides. Details of the microscopic and x-ray analyses are described in Appendix B. Fraction 4 was studied by direct probe MS and found to be predominantly elemental sulfur (S<sub>8</sub>) with a small amount of AA which was probably trapped in the adherent layer of sulfur.

The gravimetric results of the liquid column chromatographic fractionation of the chloroform soluble portion of the combusted red smoke mix are shown in Table 2. These bands were analyzed also by combined GC/MS as well as GC alone. Band 1, the red band, was essentially pure MAA, as was the corresponding band of the uncombusted smoke. However, this band comprised only 86 percent of the total put on the column as compared to 98 percent for the uncombusted smoke mix. Band 2, the orange component, was very nearly pure AA, again corresponding to the same band of the original mix. However, in the combusted mix, this



band accounted for 6 percent of the total, a ten-fold increase from the original mix. Since this portion has an orange color, it is probably 1-AA,<sup>(6)</sup> which would indicate that some demethylation takes place during combustion. This band also contained some MAA and another AA, which would have to be 2-AA, a yellow compound,<sup>(6)</sup> since there can be only the two isomers. Band 3, which is about five-fold greater than the corresponding band of the uncombusted mix, contained the two isomers of AA, along with small amounts of MAA, an unidentified alkane and an apparent cyanoanthraquinone. The largest AA peak coelutes in the gas chromatogram with two minor components which consequently could not be identified. The main components in band 4 are the two AA's, four compounds tentatively identified as aliphatic amides, a phthalate and two other compounds whose identities could not be established. A summary of the comparative compositions of the uncombusted and combusted smoke mixes is shown in Table 3.

A second column chromatographic separation was carried out and the major yellow portion of band 3 was isolated. This portion, labeled band 3b contained about 4 percent of the sample chromatographed. Carbon-13 NMR analyses of bands 2 and 3b indicated structures consistent with 1-AA and 2-AA, respectively.

Solubility tests on the combusted smoke mix revealed that the chloroform soluble portion represented 94 percent of the total material. Thirty-five percent of the chloroform insoluble residue was extracted with water, which corresponds to 2.5 percent of the original particulate material being water soluble. In a direct test of the water solubility of the whole combusted smoke, 3.5 percent was extracted into water, which correlates well with the value of 2.5 percent above, but a trace amount of the red MAA was also dissolved into the water.

The UV and visible spectra of the combusted and non-combusted red smoke mixes were virtually identical. The visible spectra were essentially the same as that of MAA,<sup>(2)</sup> with a maximum at a wavelength of 508 nm. The ultraviolet spectra had a large maximum at 247 nm and much smaller maxima at 275 and 315 nm.

Vapor phase samples were collected on Tenax-GC and XAD-2 traps as described in Appendix C. The material adsorbed on the Tenax was analyzed, after thermal desorption,<sup>(5)</sup> first by capillary column GC and then by GC/MS. When the two Tenax traps were analyzed by GC, it was found that they were both qualitatively alike, although they differed quantitatively. Consequently, only one sample, the one taken at the later time period, was analyzed by GC/MS. The gas chromatogram of this sample is shown in Figure C-1. Temperature programming started at the twenty minute point after desorption into a liquid nitrogen trap. A list of compounds showing tentative identifications is presented in Table 4. The major components in the red smoke mix are the toluene, styrene, chloromethylbenzene and several of the alkanes. In general, the alkanes seemed to be of the order of C<sub>9</sub> to C<sub>12</sub> and larger. In many instances chromatographic peaks were not well resolved, as can be seen in Figure 1, which made MS identification very difficult, if not impossible. The compounds listed below the alkanes in Table 4 were present in relatively minor quantities, i.e., between 5 and 10 percent

TABLE 3. SUMMARY OF COMPARATIVE COMPOSITION OF  
UNCOMBUSTED AND COMBUSTED RED SMOKE MIX<sup>a</sup>

		Component	
		Uncombusted	Combusted
A. Vacuum Sublimation			
<u>Fraction</u>			
1	<i>1-MAA</i> anthraquinone		<i>1-MAA</i> AA Sulfur
2	<i>1-MAA</i>		(a) <i>1-MAA</i> AA (b) <i>1-AA</i> <i>1-MAA</i> Sulfur
3	<i>Carbonaceous matter</i> MAA		<i>Carbonaceous matter</i> KCl NaCl Sulfur Trace metals
4			<i>Sulfur</i> AA
B. Silica Gel Chromatography			
<u>Band</u>			
1	<i>1-MAA</i>		<i>1-MAA</i>
2	<i>1-AA</i> <i>1-MAA</i> Hydrocarbon Siloxanes		<i>1-AA</i> <i>1-MAA</i>
3	AA <i>Aliphatic amide</i> Hydrocarbons Cyclic or unsaturated hydrocarbon other amides		<i>2-AA</i> <i>1-AA</i> Cyanoanthraquinone Hydrocarbon <i>1-MAA</i>
4			<i>2-AA</i> <i>1-AA</i> Aliphatic amides Phthalate

<sup>a</sup>Major components in italics (> 20%).

Abbreviations: MAA - Methylaminoanthraquinone  
AA - Aminoanthraquinone

TABLE 4. TENTATIVE IDENTIFICATION OF VAPOR-PHASE COMBUSTION PRODUCTS OF RED AND VIOLET SMOKE MIXES BY TENAX TRAPPING<sup>a</sup>

<u>Red</u>	<u>Violet</u>
<i>Toluene</i>	<i>Carbon disulfide</i>
<i>Styrene</i>	<i>C<sub>2</sub> Benzene</i>
<i>Chloromethylbenzene</i>	<i>Toluene</i>
Alkanes	C <sub>3</sub> Benzene
Benzaldehyde	Alkanes
Dichlorobenzene	C <sub>4</sub> Benzene
Phenol	C <sub>2</sub> Thiophene
Cyano-benzene	Acetophenone
Acetophenone	Phenylacetaldehyde
Phenylacetylene	
C <sub>10</sub> Alkene	
Naphthalene	
Benzothiophene	
C <sub>8</sub> Benzene	
Biphenyl/Acenaphthene	

<sup>a</sup>Major components in italics (> 20%).

as large as the toluene peak, while a number of other constituents not listed were present in even smaller quantities.

The XAD traps were extracted with methylene chloride overnight, but the extracts were accidentally evaporated to dryness for an indeterminate length of time and therefore could not be analyzed.

Samples for particulate size determinations were collected by a conventional eight stage cascade impactor by drawing air from the chamber at a rate of 1 L/min. The weights of particulate per stage were determined spectrophotometrically using the whole combusted smoke mix as the calibration standard. Details of the procedure are given in Appendix D. The gravimetric data upon which the particle diameters are calculated are presented in Table D-1. The particle size relationships for the combusted red smoke mix are shown in Figure D-1. The mass median diameter of the red smoke mix taken seven minutes after ignition is 2.2  $\mu$ m, and this parameter increases to 2.7  $\mu$ m at twenty-six min after ignition. The geometric standard deviations,  $\sigma_g$ , are both 1.6.

#### Violet Smoke Mix

Uncombusted. The violet smoke mix is formulated to contain 80 percent DDA and 20 percent MAA.<sup>(3)</sup> The uncombusted violet smoke mix, Lot RJC31-123 was first separated into four fractions by the differential solubility procedure described previously.<sup>(1,2)</sup> The weight percentages of the fractions from the violet mix were very similar to those of the original smoke mix (VSM) as shown in Table 1.

These fractions were first examined by TLC. Fractions 1 and 2 each had MAA, DDA and DAA bands. Fraction 1 had light yellow and light orange fluorescent bands ( $\lambda_{ex}$  254 nm) just below the MAA band, and another yellow band nearer the origin. This latter band was also detected in the DDA standard. Fraction 2 had a light purple band about midway on the plate as the only impurity. The most prominent line in fraction 3 was DAA, but there were three impurities detected, including a rust colored line near the solvent front, a fluorescent orange line corresponding to the one in fraction 1, and a visible yellow line about half way in the chromatogram which had a bright blue fluorescence.

Fractions 1 and 2 were analyzed by GC/MS. Fraction 2 was also analyzed by direct probe MS, as were fractions 3 and 4. The major constituent of fraction 1 was MAA. Very minor quantities of azobenzene and anthraquinone were detected as well along with trace quantities of several other components, most of which appeared to be hydrocarbons. Fraction 2 was predominately MAA with some DDA and DAA. No other components were detected in this fraction. Fraction 3 was composed of MAA, DDA and DAA with no impurities detectable.

The direct probe mass spectrum of fraction 4, the extraction residue, indicated that major compounds present were DDA and DAA, although these compounds would be expected to have been completely dissolved after twenty-four hours extraction in a Soxhlet extractor. Previous experience<sup>(1,2)</sup> had indicated that this fraction would have contained mainly hydrocarbon residues, but in this case the hydrocarbon spectra (if any hydrocarbons were present) were masked in the predominance of DDA and DAA. The DAA was most likely an oxidation product of the DDA upon drying this fraction, as the original DAA present was dissolved very early in the extraction.

Combusted. Previous reports have indicated that oxidation of the violet smoke mix converts the DDA to DAA.<sup>(1,3)</sup> This can be detected simply by visual observation of the combusted product. The uncombusted smoke mix is a brownish appearing powder that is light yellow in a dilute solution. The combusted material, however, is a purple powder that is also purple in a dilute solution. The visible spectra of both smoke mixes are shown in Figure 1. It can be seen that there is a shift of the visible spectrum toward the higher wavelengths indicative of DAA. Because of the presence of 20 percent of MAA, the spectra are somewhat different from those of pure DDA and DAA shown in Figure 2 and indicated by the increased absorbance of the original mix above 500 nm. The ultra violet spectra show a shift to lower wavelengths after combustion. The uncombusted mix has a maximum of 252 nm, and a shoulder at 280 nm, while the combusted mix has a maximum at 246 nm and a much less noticeable shoulder.

Because MAA and DAA have similar solubilities, the differential solubility technique could not be used to fractionate the combusted smoke mix as was done with the original smoke mix. Therefore, the chloroform soluble portion of the sample was chromatographed on a silica gel column by open column liquid chromatography in the same manner as the red smoke mix. Five bands were obtained by this procedure, the fifth band being the material first eluted by acetone and

then by methanol. Even after this treatment a small amount of a red substance remained on the column, as well as some black material at the head of the column.

The column bands were sufficiently volatile to be analyzed by GC/MS. Band 1 was essentially pure MAA. The major component of band 2 was AA, again probably 1-AA because of the orange color.<sup>(6)</sup> There were small amounts of MAA, a phthalate and an alkene present also. Band 3 consisted of ten to twelve components, the largest one being an apparent C<sub>12</sub> hexene or olefin. Other components include MAA, AA, another methylaminoanthraquinone (2-MAA), a cyanoanthraquinone and several hydrocarbons. Band 4 is essentially pure DAA. Band 5 again consists of about a dozen components, the largest of which is a complex molecule of mass 157 and appearing to have the formula C<sub>9</sub>H<sub>19</sub>ON. Other constituents are phthalic anhydride, AA, DAA, several hydrocarbons and apparent aliphatic amides, a phthalate, plus six unidentified compounds.

A summary of the composition of the uncombusted and combusted violet smoke mixes is shown in Table 5. Because the two materials could not be analyzed by the same procedure, a direct fraction to fraction comparison cannot be made. The insoluble residue would be expected to have essentially the same composition qualitatively as that from the red smoke mix. Solubility tests showed that the chloroform soluble portion of the combusted violet smoke mix represented 83 percent of the total. When the chloroform insoluble residue was extracted, 24 percent of this portion was soluble in water. Thus, about 4 percent of the total particulates are water soluble. A direct measurement of water solubility was not done because of the small amount of material collected. Under the assumption that the residues of the combusted violet and red smoke mixes would be similar, the violet smoke mix residue was not examined by microscopic and x-ray techniques.

Vapor phase samples from the violet smoke test were collected and analyzed in the same manner as described above for the red smoke mix, and a detailed description is given in Appendix C. The gas chromatograms of the material from the Tenax traps again were qualitatively alike so that only one sample was analyzed by GC/MS. The gas chromatogram is shown in Figure C-2 and a list of compounds showing tentative identifications is presented in Table 4. In the violet smoke vapor phase, the largest component was identified as carbon disulfide, while the next two largest were C<sub>2</sub> benzenes (possibly xylenes) and toluene was next in quantity. The other compounds listed in Table 4 from C<sub>3</sub> benzene on were present in relatively small amounts, i.e., between 5 and 10 percent of the carbon disulfide, while a number of other, non-listed compounds were present only in trace quantities.

The XAD from the traps was extracted overnight with methylene chloride in Soxhlet extractors. These extracts were then evaporated under flowing nitrogen and with natural evaporative cooling, to a volume suitable for injection into the GC/MS. A list of compounds that were tentatively identified is shown in Table 6. The largest constituent in the XAD extract was naphthalene, while several C<sub>1</sub> indanes and C<sub>4</sub> benzenes were next largest. Those compounds in Table 6 listed

TABLE 5. SUMMARY OF COMPARATIVE COMPOSITIONS OF  
UNCOMBUSTED AND COMBUSTED VIOLET SMOKE MIX<sup>a</sup>

A. Uncombusted (Differential Solubility)

<u>Fraction</u>	<u>Component</u>
1	1-MAA DDA      Azobenzene DAA      Anthraquinone
2	1-MAA DDA DAA
3	DAA DDA 1-MAA
4	DDA (DAA) (Carbonaceous matter)

B. Combusted (Silica Gel Chromatography)

<u>Band</u>	
1	1-MAA
2	1-AA 1-MAA Phthalate Hydrocarbon
3	<i>C<sub>12</sub> Hexene or Olefin</i> 1-MAA AA 2-MAA Cyanoanthraquinone Hydrocarbons
4	DAA
5	<i>C<sub>9</sub>H<sub>19</sub>ON (Mass 157)</i> Phthalic anhydride AA DAA Hydrocarbons Aliphatic amides Phthalate

Insoluble residue: Carbonaceous matter, sulfur, KCl, NaCl

<sup>a</sup>Major component italicized (> 20%).

Abbreviations: MAA - methylaminoanthraquinone  
DDA - 1,4-diamino-2,3-dihydroanthraquinone  
DAA - 1,4-diaminoanthraquinone  
AA - aminoanthraquinone

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TABLE 6. TENTATIVE IDENTIFICATION OF VAPOR-PHASE COMBUSTION PRODUCTS  
OF VIOLET SMOKE MIX BY XAD-2 TRAPPING<sup>a</sup>

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<u>Compound</u>
<i>Naphthalene</i>
C <sub>1</sub> Indanes
C <sub>4</sub> Benzenes
Dihydronaphthalene
C <sub>6</sub> Benzene
Methylbenzoate
C <sub>1</sub> Indene
Benzothiophene
C <sub>6</sub> Benzenes
C <sub>2</sub> Indanes
C <sub>5</sub> Benzenes
C <sub>7</sub> Benzenes
Methylbenzothiophene
Methylnaphthalenes
C <sub>3</sub> Indanes
Biphenyl/Acenaphthene
C <sub>2</sub> Naphthalene
C <sub>4</sub> Indanes
Methylbiphenyls

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<sup>a</sup>Major components in italics (> 20%).

listed below C<sub>4</sub> benzene were present in relatively small quantities, i.e., between 5 and 10 percent of the naphthalene. As with the Tenax samples a number of other compounds were present in trace quantities, and overlapping of chromatographic peaks made MS identification difficult.

Samples for particulate size analysis were collected and analyzed in the same manner as for the red smoke mix as described above. Details of this procedure are given in Appendix D. The particle size relationships are shown in Figure D-2. The mass median diameter of the particles collected two minutes after ignition are 1.1  $\mu\text{m}$ , and of those collected twenty-eight minutes after ignition are 2.4  $\mu\text{m}$ . The geometric standard deviations,  $\sigma_g$ , are 2.1 and 2.4, respectively. The particle size does show some evidence of growth with time, but it must be remembered that these particulates were confined in a chamber and subjected to convectional currents generated by solar heating on the exterior of the chamber. Under field conditions, the particles would be increasingly dispersed with time.

## SUMMARY AND CONCLUSIONS

As expected, the combusted smoke mixes were found to differ in composition from the original mixes. Methylaminoanthraquinone (MAA) made up 98 percent of the red smoke mix. It accounted for 86 percent of the chloroform soluble particulate matter in the smoke produced when the red smoke grenade was combusted. Aminoanthraquinones (1-AA and 2-AA) were found in the aerosolized combustion products at a ten percent level, a more than ten-fold increase over their concentration in uncombusted red smoke mix. Inorganic materials from the grenade charge, including potassium and sodium chlorides, elemental sulfur, and trace metals, were also detected in the particulate phase of the combustion products. The vapor phase constituents identified in the combusted smoke mix were primarily toluene, styrene, and chloromethylbenzene, with smaller amounts of aliphatic and aromatic hydrocarbons, substituted benzenes, and benzo thiophene.

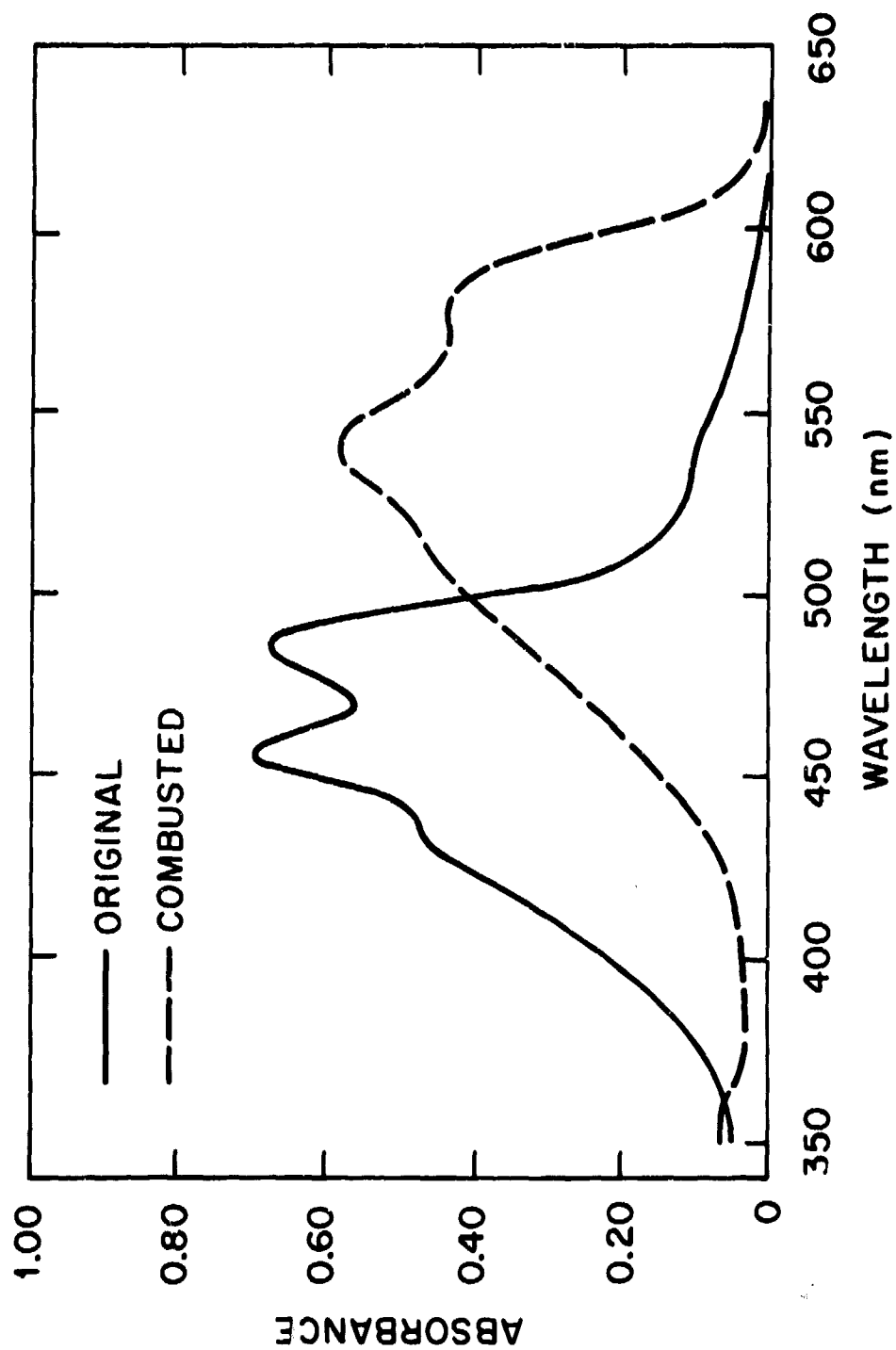
The original violet mix, formulated to contain 1,4-diamino-2,3-dihydroanthraquinone (DDA) and MAA, was found to contain, in addition to those two components, some 1,4-diaminoanthraquinone (DAA), as well as smaller amounts of azobenzene and anthraquinone. After combustion, DDA was found to have been converted almost quantitatively to DAA. As in the combusted red smoke mix, both MAA and AA were detected in the combusted violet smoke mix along with smaller amounts of other organic compounds including cyanoanthraquinone, aliphatic hydrocarbons and amides, and phthalates. Inorganic compounds detected included potassium and sodium chlorides, sulfur, and trace metals. Vapor phase components trapped during the combustion of violet smoke mix included carbon disulfide, alkyl benzenes, alkanes, thiophenes, acetophenone, and phenylacetaldehyde.

The major chemical transformations observed in both the red and the violet smoke mixes, DDA going to DAA and MAA converting partially to 1-AA and 2-AA, were both in the direction of increased biological activity. Previous work at our laboratory<sup>(2)</sup> showed that DAA is much more active in the Ames Salmonella assay than is its precursor, DDA. In a bioassay conducted for the National Cancer Institute,<sup>(7)</sup> 2-AA was found to be carcinogenic in both rats and mice.

A number of the compounds observed in the combustion products could be only tentatively identified. Some of these, such as cyanoanthraquinones and amides have potential for biological activity. It would be necessary to isolate greater quantities than was possible in the current study if more detailed spectroscopic identification or biological testing of these components were thought appropriate.

The results of this study lead to the conclusion that, if there is a significant risk of human exposures to colored smokes, it is important to fractionate and chemically characterize the combustion products for the purpose of health effects evaluation and, if new components of unknown biological activity are found in the combustion products, to prepare samples for toxicity testing.

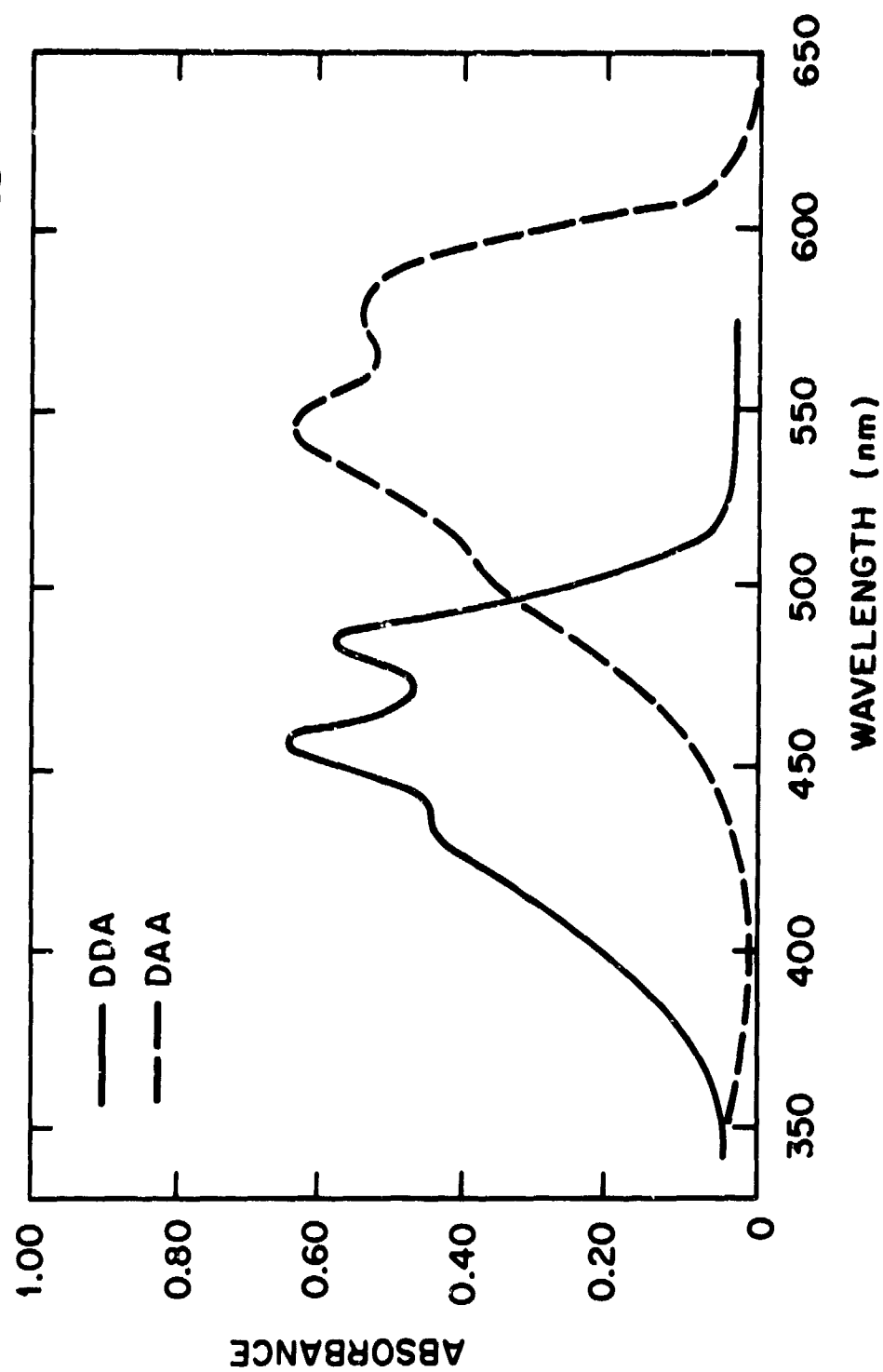




VISIBLE SPECTRA OF VIOLET SMOKE MIXES

Figure 1

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VISIBLE SPECTRA OF DDA AND DAA

Figure 2

#### LITERATURE CITED

1. Rubin, I.B., M.V. Buchanan and G. Olerich. 1982. The preparative scale separation and identification of constituents of anthraquinone-derived dye mixtures. Part 1. 1-Methylaminoanthraquinone, 1,4-diamino-2,3-dihydroanthraquinone and 1,4-diaminoanthraquinone. Anal. Chim. Acta, 135:111-119.
2. I.B. Rubin and M. V. Buchanan. 1980. Chemical Characterization of Army Colored Smoke Mixes (Red, Violet, Yellow and Green). Oak Ridge National Laboratory, Oak Ridge, TN. Report to US Army Medical Bioengineering Research and Development Laboratory, Frederick, MD.
3. Owens, E.J. and D.M. Ward. 1974. A Review of the Toxicity of Colored Smokes and Colored Smoke Dyes. AD A003827. Chemical Systems Laboratory, Aberdeen Proving Ground, MD.
4. Buchanan, M.V. 1982. Mass spectral characterization of nitrogen-containing compounds with ammonia chemical ionization. Anal. Chem., 54:570-574.
5. Higgins, C.E. 1981. Preparation of polar glass capillary columns. Anal. Chem., 53:732-734.
6. Franc, J. and M. Hajkova. 1964. Separation and determination of aminoanthraquinones by means of thin-layer chromatography. J. Chromatogr., 16:345-349.
7. U.S. Department of Health, Education, and Welfare. 1978. Bioassay of 2-Aminoanthraquinone for Possible Carcinogenicity. National Cancer Institute Carcinogenesis Technical Report Series No. 144, National Institutes of Health, Bethesda, MD. DHEW Publication No. (NIH) 781399.

## APPENDIX A: CHEMICAL SEPARATION SCHEMES

The schemes for the separation of the red and violet smoke mixes are given in this Appendix.

### Red Smoke Mix

The uncombusted and combusted smoke mixes were each separated into fractions using both vacuum sublimation and liquid chromatographic procedures. The uncombusted red smoke mix was separated into three fractions by means of a vacuum sublimation method described previously.<sup>(1,2)</sup> When the combusted smoke mix was separated by this procedure, it was noted that an orange substance was sublimed on top of the red MAA layer, and that a yellow, insoluble component adhered to the water cooled condenser. Therefore, the vacuum sublimation procedure was modified slightly in order to obtain the bulk of the MAA in one fraction and to concentrate the orange component into another fraction. The modified flow sheet is shown in Figure A-1. The insoluble yellow component was labeled fraction 4.

The separation of impurities in the smoke mixes from the major components by TLC on silica gel layer has been generally effective. In order to effect a better separation and concentration of minor components than that afforded by the vacuum sublimation procedure, the combusted red smoke mix was chromatographed on silica gel by open column liquid chromatography. The success of this experiment led to a similar chromatography of the uncombusted mix.

The chromatographic separation was accomplished on a 2.0 cm O.D. x 58 cm column packed with Davison Grade 950 silica gel in cyclohexane. A 100 mg sample of the chloroform soluble portion of the smoke mix was dissolved in chloroform and pipetted onto the top of the column. The column was then eluted with chloroform. The bands were collected by color. Band 1 contained the red-colored solution, and band 2, the orange-colored solution. Band 3 contained the remainder of the colored material elutable with chloroform. The reservoir was then filled with acetone, and the remainder of the elutable material stripped from the column composed band 4. For the combusted smoke sample, some pink material was retained at the head of the column after elution with acetone.

### Violet Smoke Mix

The uncombusted violet smoke mix was separated into four fractions by the differential solubility procedure described previously.<sup>(1,2)</sup>

It was apparent that the yellow-brown DDA of the original smoke mix had been oxidized to violet DAA. Because DAA has about the same solubility as MAA, rather than being relatively insoluble like DDA, the differential solubility procedure could not be used to fractionate the combusted violet smoke mix. Therefore, the combusted violet smoke mix was also separated by open column liquid chromatography using the same method as for the red smoke mix. Bands 1 and 2 were the red and orange colored solutions, respectively. Band 3 contained the eluate between the orange and purple bands, while band 4 contained the purple eluate.

The column was then developed with 900 mL of acetone, which eluted a purplish band but left behind a broad yellow band, as well as some material at the head of the column. The solvent was then switched to 300 mL of methanol which eluted a reddish purple band from the head of the column and finally the residual yellow material from the acetone elution. A reddish band still remained near the top of the column and some black material was retained at the head of the column. The total acetone and methanol eluate was combined into band 5. Upon evaporation, some of this material could not be redissolved.

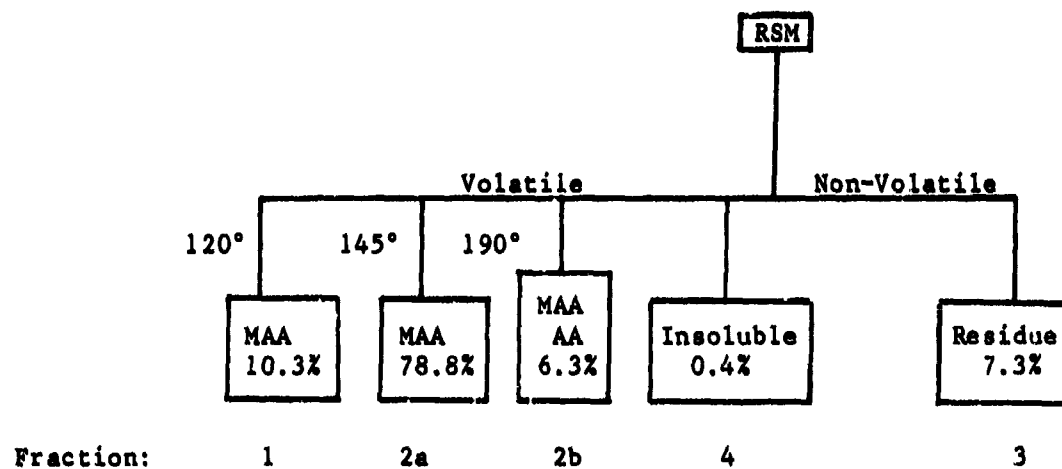


Figure A-1. Separation flow sheet for combusted smoke mix by vacuum sublimation.

## APPENDIX B. PHYSICAL ANALYSIS OF RESIDUE

The residue (non-volatile) portion of the combusted red smoke mix was examined by x-ray diffraction (XRD), x-ray fluorescence (XRF) and scanning electron microscopy (SEM). A sample of the whole residue was examined first by XRD. Potassium and sodium chlorides and silica were found. Graphitized carbon could not be detected and no crystalline sulfur compounds were found. The lattice parameter of the potassium chloride was reduced, which indicates substitution of other ions in the crystal. The water insoluble portion of the residue was also examined by XRD. A diffuse line corresponding to partially graphitized carbon was seen, but again no crystalline sulfur compounds were found. The dried water-soluble portion showed strong potassium and sodium chloride lines, and in this material the potassium chloride lattice spacing was normal, presumably because of recrystallization. The photomicrograph in the upper left of Figure B-1 shows the general morphology of the particles of the whole residue. The cylindrical particles are silica and are most likely fibers from the fiber glass extraction thimble used to collect the smoke particulates. The chlorine (upper right) and potassium (lower left) maps show coincident areas indicating that the two elements are associated, very probably as potassium chloride crystals. The sulfur map (lower right) also shows association with the same particles as the potassium and chlorine. This would indicate sulfur deposited on the chloride crystals.

The photomicrograph in the upper left of Figure B-2 shows the water-insoluble portion of the residue. The electron induced energy dispersive x-ray (EDX) spectrum (upper right) shows sulfur as the major constituent. Carbon cannot be detected by EDX. The photomicrograph in the lower left of Figure B-2 shows the dried water soluble portion of the residue. The EDX spectrum shows that the major constituents are potassium and chlorine. The electron induced EDX spectrum in the upper left of Figure B-3 is from a sample of the whole residue which is shown in the photomicrograph in Figure B-1, while the spectrum in the upper right is a  $\text{AgK}_\alpha$ -induced XRF analysis of the same specimen. It indicates the presence of iron, zinc, lead and zirconium. The lower spectra are  $\text{AgK}_\alpha$ -induced XRF analyses of the waterinsoluble portion on the left and the water-soluble portion on the right. The bromine is from the mounting tape.

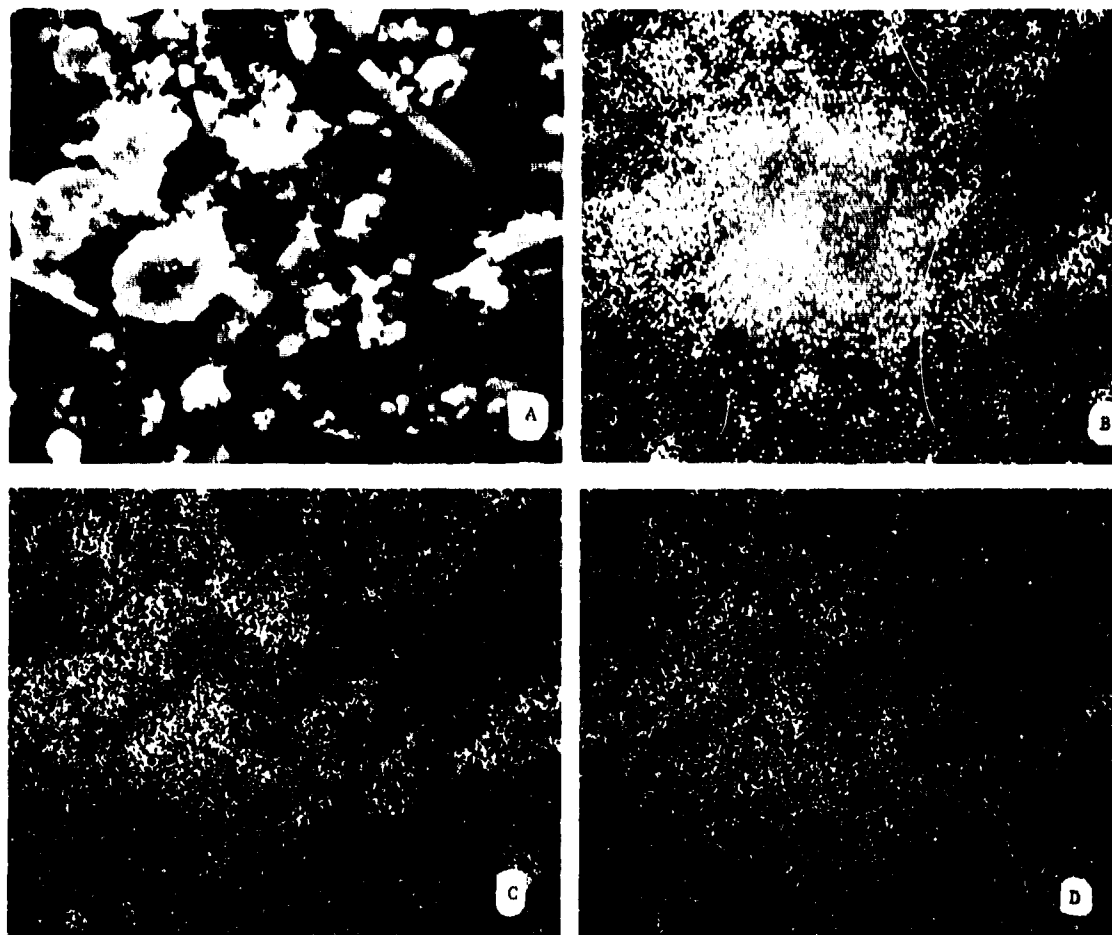


Figure B-1. Photomicrograph and Cl, K and S maps of whole unsublimed residue from red smoke mix.

- |                            |           |
|----------------------------|-----------|
| a. Photomicrograph (1600X) | b. Cl map |
| c. K map                   | d. S map  |



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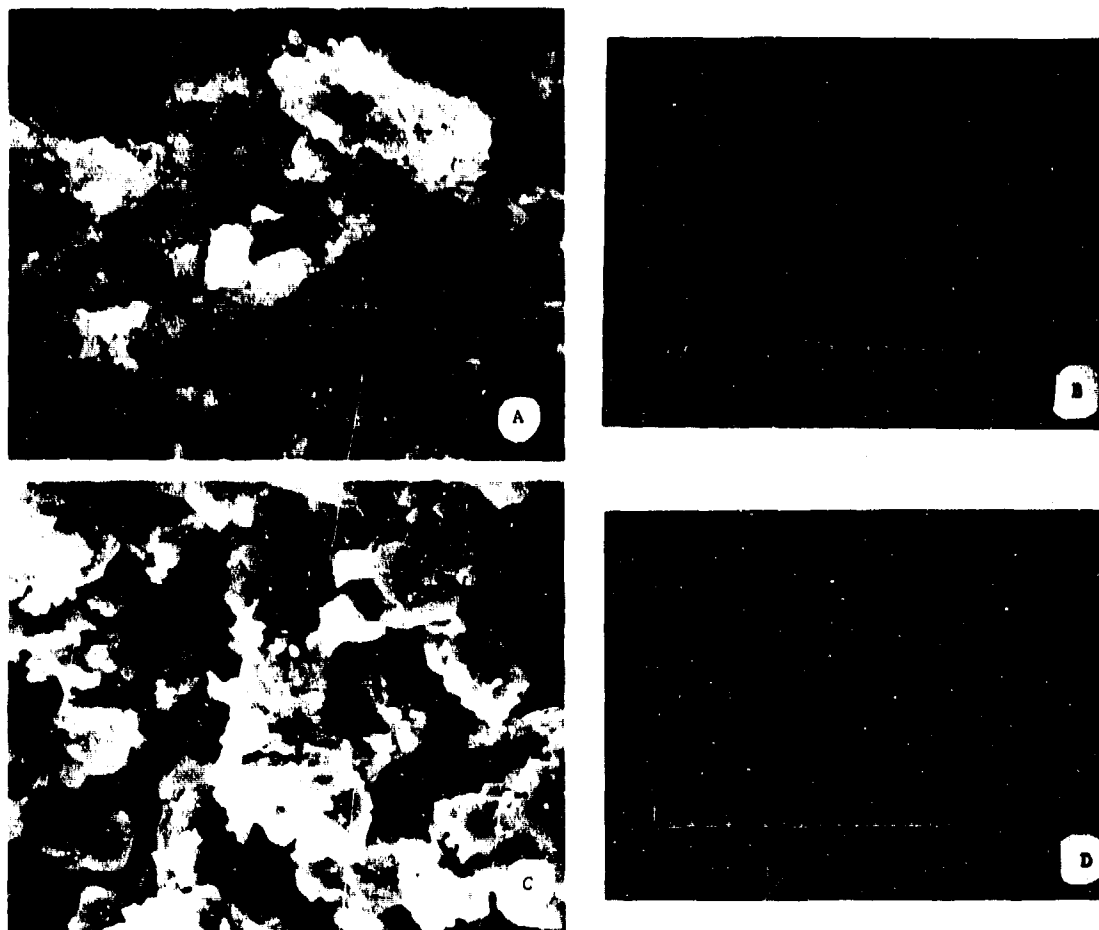


Figure B-2. Photomicrographs and EDX analyses of water soluble and insoluble portions of residue from red smoke mix.

a & b. Water insoluble portion  
c & d. Water soluble portion

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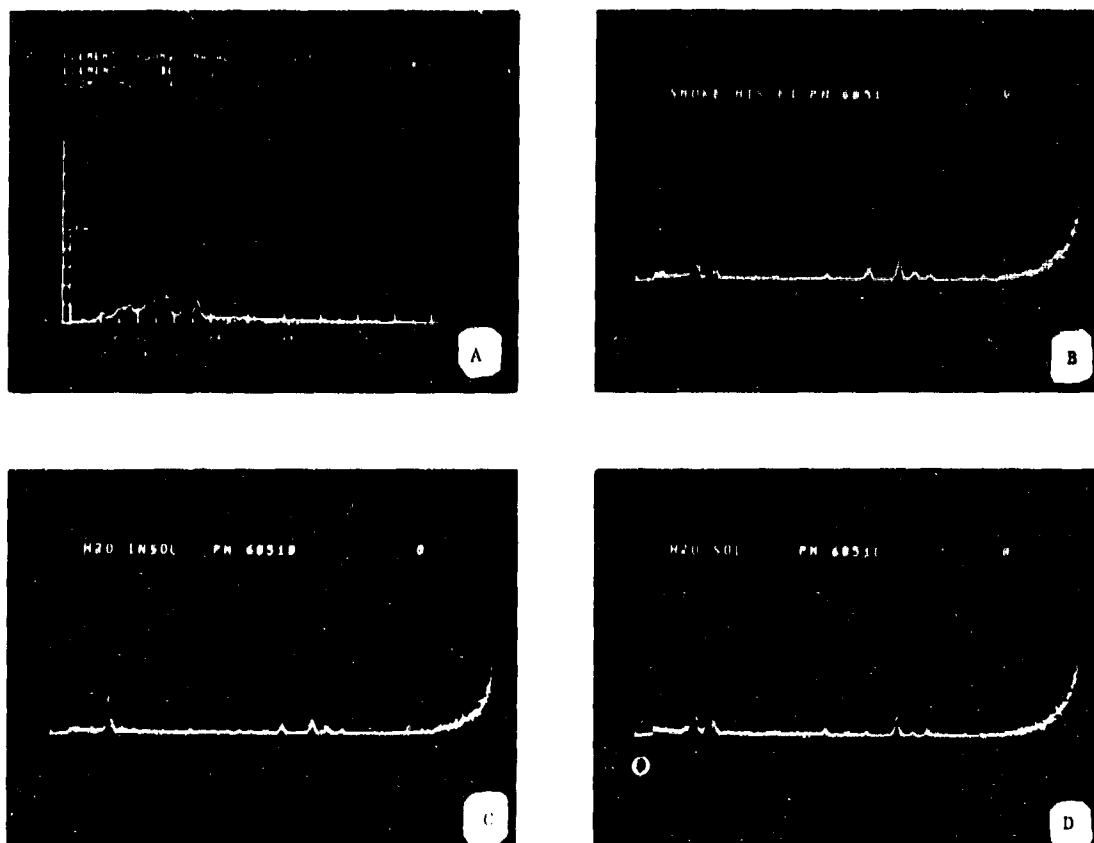


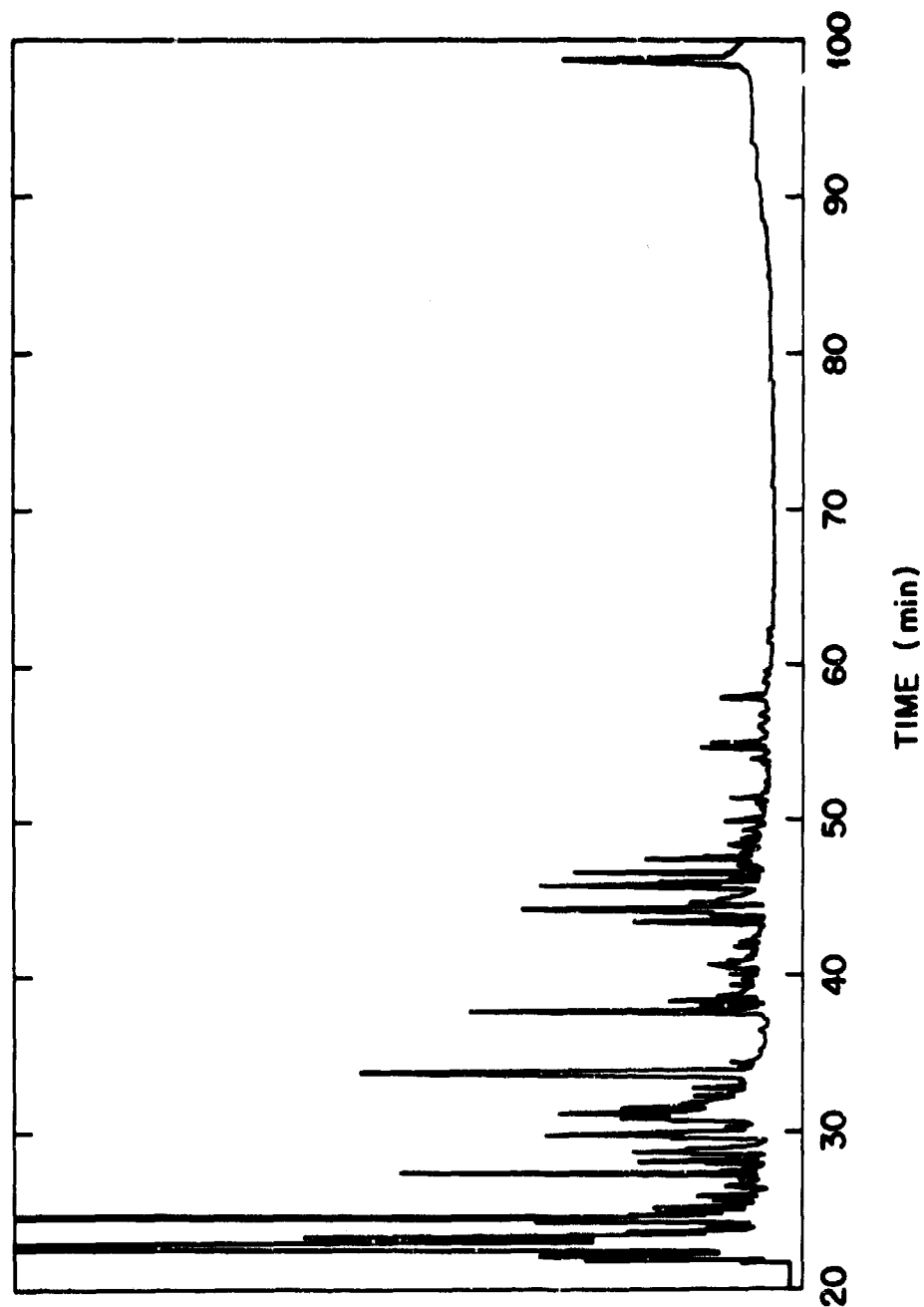
Figure B-1. EDX and XRF analyses of the residue from red smoke mix.  
a. EDX and b. XRF of whole residue  
c. XRF of water insoluble and d. water soluble portions

## APPENDIX C: VAPOR PHASE ANALYSIS

Vapor phase matter from the combustion of the red and violet smoke mixes was collected on XAD-2 and Tenax-GC traps by drawing air through the traps at a rate of 1.5 L/min for 10 min periods. The XAD-2 was pretreated by washing first with methanol and then with methylene chloride. After sample collection, the total XAD-2 was removed from the trap and transferred to a pre-extracted fiber glass extraction thimble and covered with pre-extracted glass wool. The resin was then extracted with methylene chloride in a Soxhlet extractor for 24 hours. The solution was concentrated under flowing nitrogen with natural evaporative cooling to a suitable volume for GC/MS analysis. Analysis was by electron impact MS with normal splitless injection with the GC. Temperature was programmed from 50°C to 250°C at a rate of 2°C per minute with a 5 min initial holding period.

The Tenax-GC was pretreated by washing with methanol, 50% methanol in water, ether and pentane, then extracting with pentane in a Soxhlet extractor for 24 hrs. The Tenax was then dried under nitrogen. Finally, the resin was heated to 225°C at 1°/min and activated for 24 hrs at that temperature. For sample analysis, the resin was transferred from the trap to a dish and mixed well under filtered, dry air, and approximately 100 mg was packed into a prewashed and heated piece of nominal 1/4 in O.D. glass tubing, 11 cm long. The ends of the tube were closed with prewashed and heated quartz wool. The tube was placed in the injector port of the GC which had been cooled to 75°C. The capillary stainless steel trap in front of the GC column was immersed in liquid nitrogen and the sample tube purged with helium for 20 min, while the injector port was heated to 250°C.<sup>(5)</sup> The liquid nitrogen trap was then removed and the GC/MS program was started. The oven temperature was held at 40°C for 5 min and then raised to 250°C at a rate of 2°/min.

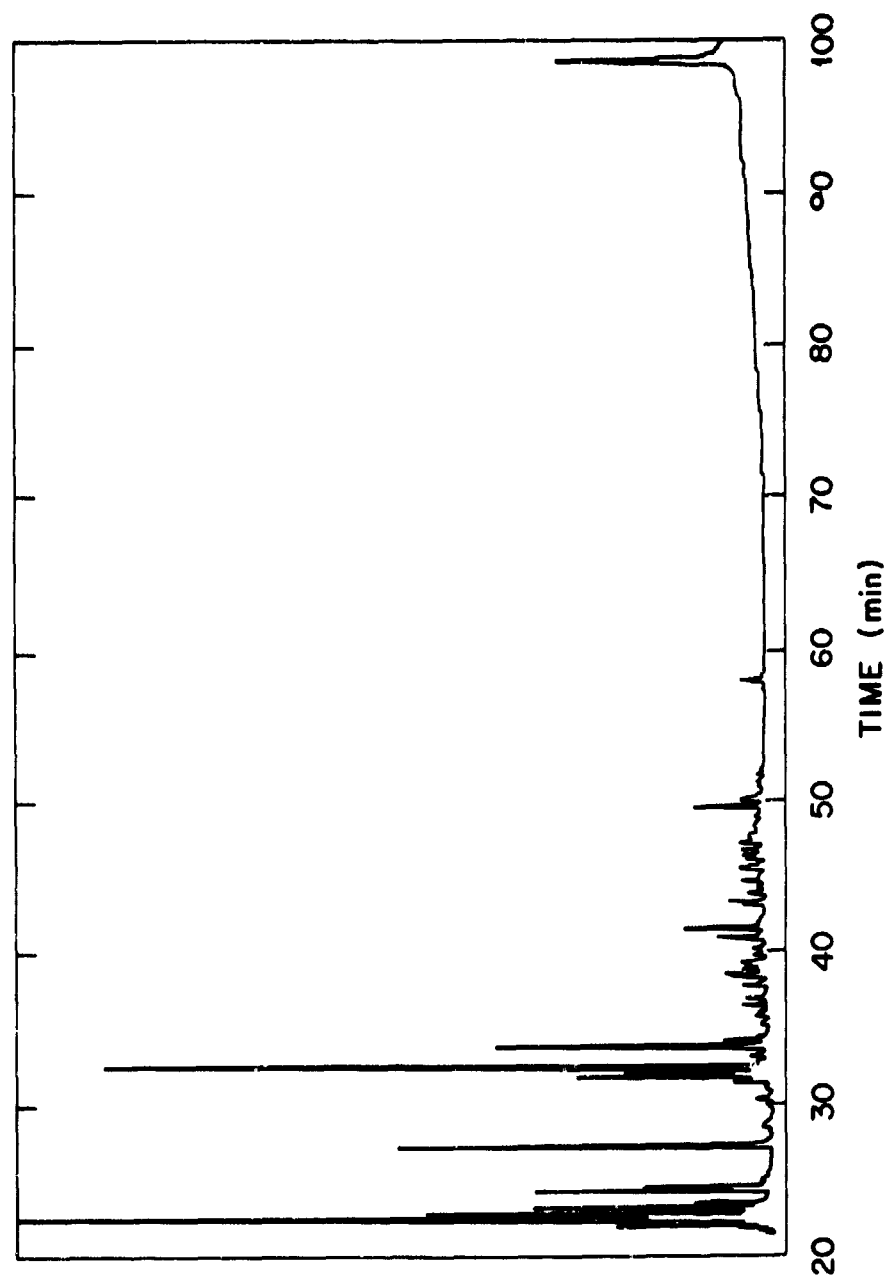
ORNL DWG 82-17520



GAS CHROMATOGRAM OF RED SMOKE MIX VAPOR-PHASE  
TRAPPED ON TENAX

Fig. C-1

ORNL DWG 82-17521



GAS CHROMATOGRAM OF VIOLET SMOKE MIX VAPOR-PHASE  
TRAPPED ON TENAX

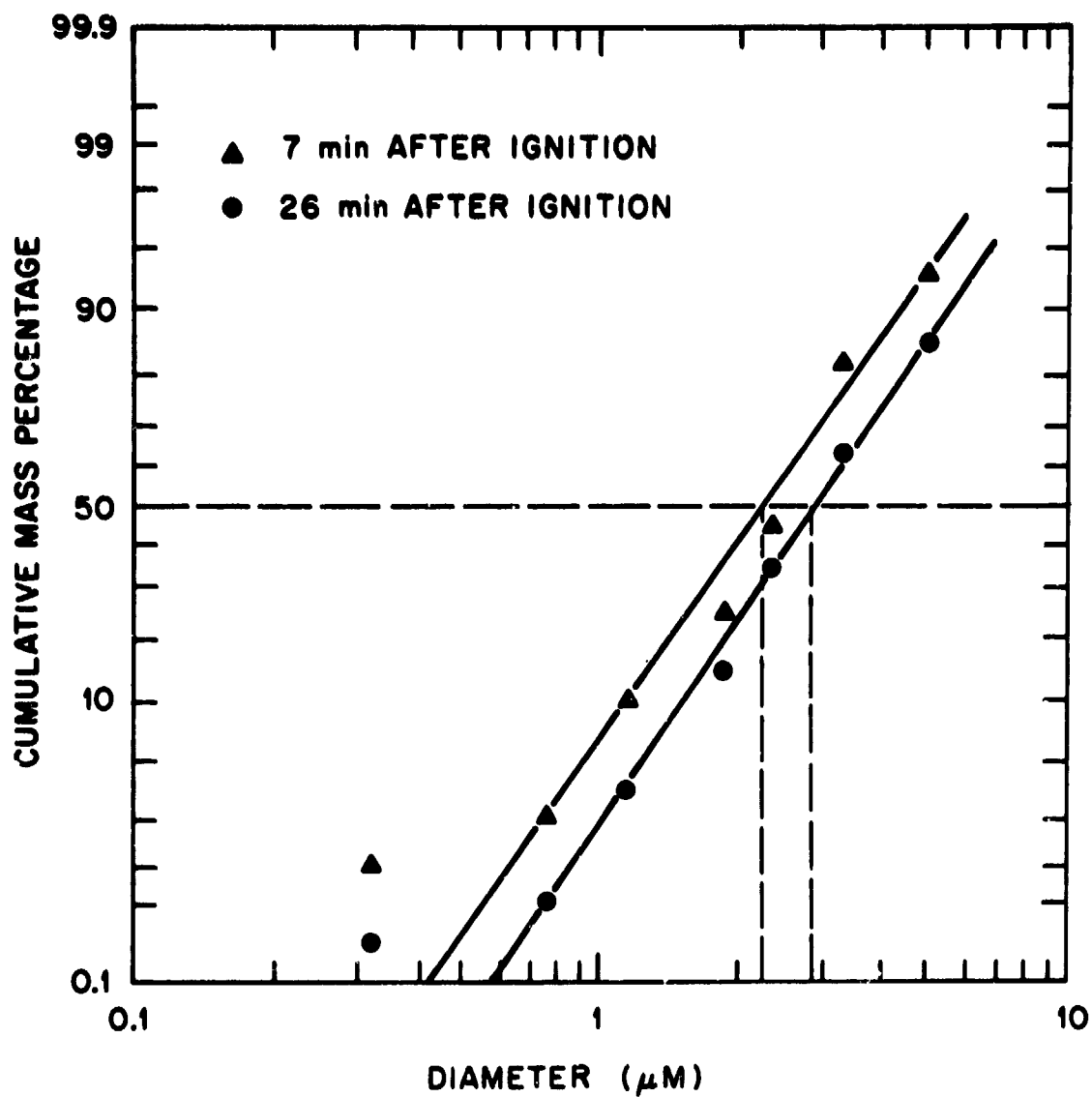
Fig. C-2

#### APPENDIX D: PARTICLE SIZE DETERMINATION

Particle size of the combusted red and violet smoke mixes was determined by sampling the interior of the combustion chamber at a rate of 1 L/min by drawing the air through a Mercer-Lovelace seven-stage cascade impactor. A standard Cambridge fiber glass filter pad was inserted at the bottom of the impactor to catch any particles small enough to escape the seventh stage and was considered as an eighth stage. The material which was trapped at the various stages of the impactor was dissolved in chloroform and, made up to a specific volume, and the absorbance was measured. Calibration curves of absorbance versus concentration for each smoke mix were prepared from the whole combusted dye mix taken from the glass trays so that no corrections had to be made for insoluble matter. The red solutions were measured at 508 nm, and the violet solutions at 542 nm. Mass median particle diameter was calculated from the results of the absorbance measurements. The weights of the particulate matter per stage are given in Table D-1.

TABLE D-1. WEIGHT VALUES FOR PARTICLE SIZE DETERMINATION  
OF RED AND VIOLET COMBUSTED SMOKE MIX

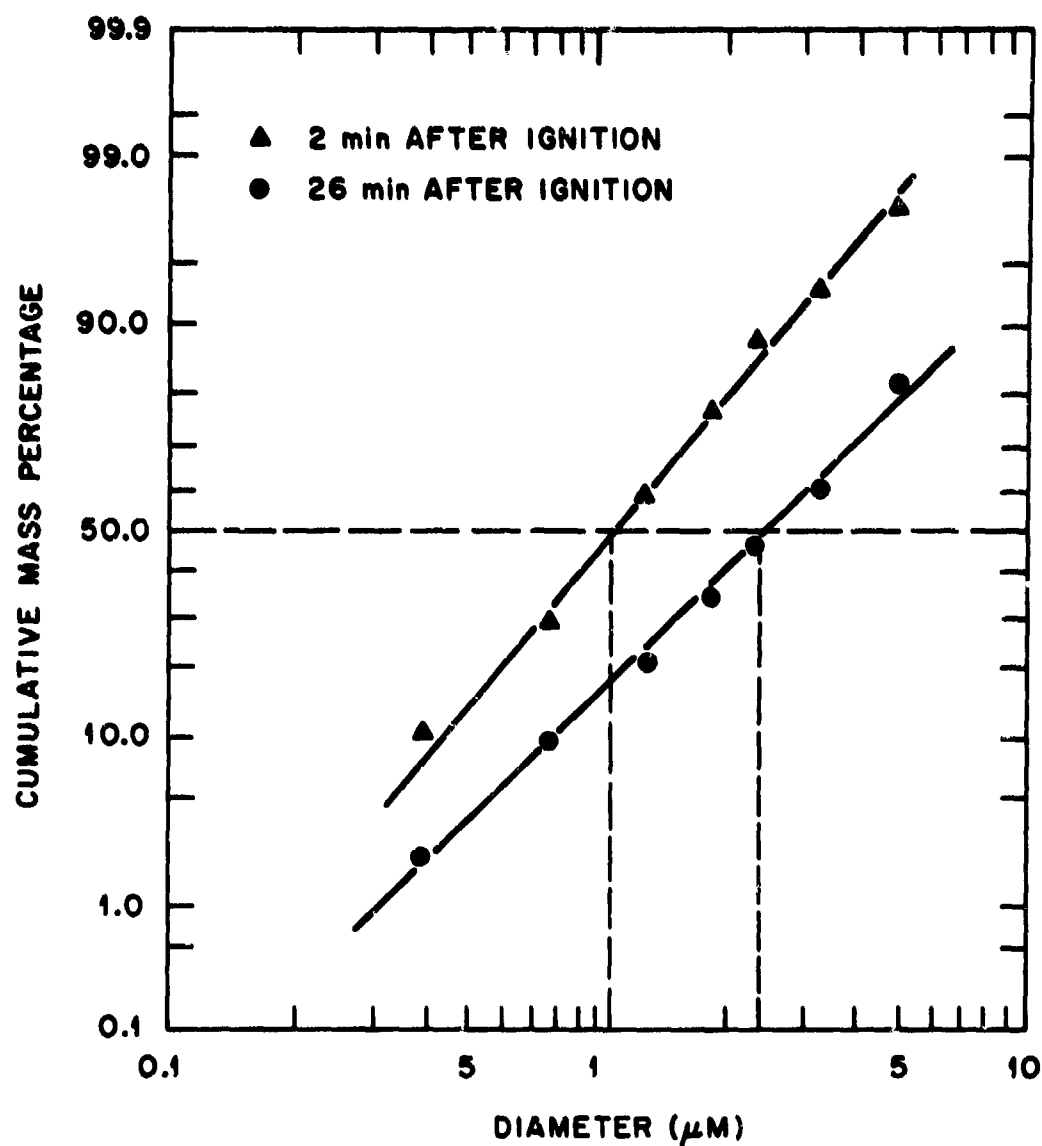
Experiment	1		2	
A. Red Smoke Mix				
Stage	Particulates, mg/stage	Cumulative Percent	Particulates, mg/stage	Cumulative Percent
1	0.22	100	0.051	100
2	0.38	92.9	0.067	83.9
3	1.11	80.8	0.088	62.8
4	0.61	45.2	0.060	35.0
5	0.44	25.6	0.040	16.1
6	0.28	11.5	0.009	3.5
7	0.05	2.6	0.001	0.6
8	0.03	1.0	0.001	0.3
B. Violet Smoke Mix				
1	0.016	100	0.048	100
2	0.031	97.8	0.058	82.2
3	0.038	93.6	0.038	60.6
4	0.080	88.4	0.032	46.5
5	0.132	77.4	0.035	34.6
6	0.224	59.4	0.032	21.6
7	0.132	28.7	0.020	9.7
8	0.078	10.7	0.006	2.2



## PARTICLE SIZE ANALYSIS OF COMBUSTED RED SMOKE MIX

Fig. D-1





PARTICLE SIZE ANALYSIS OF COMBUSTED VIOLET  
SMOKE MIX

Fig. D-2

# LIST OF ABBREVIATIONS

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AA	Aminoanthraquinone
DAA	1,4-Diaminoanthraquinone
DDA	1,4-Diamino-2,3-dihydroanthraquinone
MAA	1-Methylaminoanthraquinone
RSM	Previously analyzed red smoke mix
VSM	Previously analyzed violet smoke mix
GC	Gas chromatography
MS	Mass spectrometry
GC/MS	Combined gas chromatography and mass spectrometry
DIP MS	Direct insertion probe mass spectrometry
TLC	Thin layer chromatography
NMR	Nuclear magnetic resonance spectrometry
SEM	Scanning electron microscopy
EDX	Energy dispersive X-ray
XRD	X-ray diffraction
XRF	X-ray fluorescence
$\mu\text{m}$	Micrometers (microns)
nm	Nanometers

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#### PERSONNEL

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M. V. Buchanan  
R. W. Holmberg  
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I. B. Rubin

#### PUBLICATION

The following publication resulted from the work described in this report:

Buchanan, M. V., I. B. Rubin, and J. H. Moneyhun. Compositional Changes in Red and Violet Smoke Mixes After Combustion. Proceedings, Smoke/Obscurants Symposium VII (Unclassified Section), Harry Diamond Laboratories, Adelphi, MD, 26-28 April 1983. Project Manager, Smoke/Obscurants, Aberdeen Proving Ground, MD. (In Press)

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